

WHAT IS CLAIMED IS:

1. A process to produce a predictive data set which can be used to predict the amount of target constituent in an electrolyte solution, said process comprising:
 - (a) obtaining a sample set, wherein each sample comprises an electrolyte solution of known composition;
 - (b) obtaining an electroanalytical response for each said sample to produce a electroanalytical response data set;
 - (c) obtaining a training set that comprises said sample set and corresponding said electroanalytical response data set;
 - (d) analyzing said training set using decomposition and multivariate regression method to produce a regression data set; and
 - (e) validating said training data set to produce said predictive data set for a predictive calibration model.
2. A process according to claim 1, wherein said electrolyte solution is an electroplating bath.
3. A process of claims 2, wherein said electroplating bath comprises a plating bath of one or more metals selected from the group consisting of Cu, Sn, Pb, Zn, Ni, Ag, Cd, Co, Cr, and/or their alloys.
4. A process according to claim 1, wherein said electrolyte solution is an electroless plating bath.
5. A process of claim 4, wherein said electroless plating bath comprises an autocatalytic plating bath of one or more metals selected from the group consisting of Cu, Sn, Pb, Ni, Ag, Au, and/or their alloys.

6. A process of claim 4, wherein said electroless plating bath comprises an immersion plating bath of one or more metals selected from the group consisting of Cu, Sn, Pb, Ni, Ag, Au and/or their alloys.
7. A process according to claim 1, wherein said electrolyte solution is an electrowinning bath.
8. A process of claims 7, wherein said electrowinning bath comprises a plating bath of one or more metals selected from the group consisting of Cu, Sn, Pb, Zn, Ni, Ag, Cd, Co, Cr, and/or their alloys.
9. A process according to claim 1, wherein said electrolyte solution is an electrorefining bath.
10. A process of claims 9, wherein said electrorefining bath comprises a plating bath of one or more metals selected from the group consisting of Cu, Sn, Pb, Zn, Ni, Ag, Cd, Co, Cr, and/or their alloys.
11. A process according to claim 1, wherein said electrolyte solution is an electroforming bath.
12. A process of claims 11, wherein said electroforming bath comprises a plating bath of one or more metals selected from the group consisting of Cu, Sn, Pb, Zn, Ni, Ag, Cd, Co, Cr, and/or their alloys.
13. A process according to claim 1, wherein said electrolyte solution is an electromicromachining bath.

14. A process of claims 13, wherein said electromicromachining bath comprises a plating bath of one or more metals selected from the group consisting of Cu, Sn, Pb, Zn, Ni, Ag, Cd, Co, Cr, and/or their alloys.

15. A process according to claim 1, wherein said electrolyte solution is an electropolishing bath.

16. A process according to claim 1, wherein said sample data set of step (a) is obtained by design of experiment (DOE) routines.

17. A process according to claim 16, wherein said DOE routine is multicomponent multilevel linear orthogonal array.

18. A process according to claim 16, wherein said DOE routine is multicomponent multilevel fractional factorial.

19. A process according to claim 1, wherein the electroanalytical response of step (b) is obtained by DC Voltammetry selected from the group consisting of:

DC cyclic Voltammetry;

DC Linear Scan Voltammetry;

DC Anodic Stripping Voltammetry;

DC Cathodic Stripping Voltammetry;

DC Adsorptive Stripping Voltammetry;

DC Cyclic Voltammetric Stripping technique;

DC Staircase Voltammetry;

and combinations thereof.

20. A process according to claim 1, wherein the electroanalytical response of step (b) is obtained by a technique selected from the group consisting of:

Normal Pulse Voltammetry;
Reverse Pulse Voltammetry;
Differential Pulse Voltammetry;
Square Wave Voltammetry;
AC Voltammetry;
Chronoamperometry;
Chronopotentiometry;
Electrochemical Impedance Spectroscopy technique;
Polarographic techniques;
and combinations thereof.

21. A process according to claim 1, wherein said electroanalytical response of step (b) comprises a plurality of data points.

22. A process according to claim 1, wherein said electroanalytical response of step (b) is a combination of one or more portions of a complete electroanalytical response.

23. A process according to claim 1, wherein said electroanalytical response of step (b) comprises a combination of one or more portions of independent electroanalytical responses.

24. A process according to claim 1, wherein said regression data set of step (d) is obtained by a technique selected from the group consisting of:

sequential decomposition followed by a multivariate regression (PCR);
simultaneous decomposition and regression (PLS);
internal validation;
external validation;
and combinations thereof.

25. A process according to claim 24, wherein said internal validation uses cross validation comprising the following steps:

- (a) omitting a single sample from said training set, thereby creating a new training set;
- (b) analyzing said new training said using decomposition and multivariate regression method to produce a new regression data set;
- (c) predicting said omitted sample target component concentration using said new regression data set;
- (d) returning sample to the training set;
- (e) repeating steps (1) through (4) until all individual samples were treated;
- (f) determining an R^2 value for said predicted samples based on said predicted and said known concentrations;
- (g) validating said training data set if said R^2 value is above about 0.95; and repeating steps (a) to (f) if said R^2 value is less than about 0.95.

26. A process according to claim 25, wherein said internal validation uses cross validation comprising the following steps:

- (a) obtaining a second sample set comprises an electrolyte solution of known composition;
- (b) obtaining an electroanalytical response for each sample of said second sample set;
- (c) predicting said target component concentration for each sample of said second sample set using said predictive calibration model;
- (d) determining an R^2 value for all samples of said second sample set based on said predicted and said known concentrations;
- (e) validating said predictive calibration model if said R^2 value is above about 0.95; and repeating steps (a) to (e) if said R^2 value is less than about 0.95.

27. A process of producing a calibration data set to predict the amount of a target constituent in electrolyte solution, the process comprising:

(a) obtaining a sample set, wherein each sample comprises an electrolyte solution of known composition;

(b) obtaining an electroanalytical response for each said sample to produce an electroanalytical response data set;

(c) obtaining a training set that comprises said sample set and corresponding said electroanalytical response data set;

(d) preprocessing of training set;

(e) determining the calibration range;

(f) detecting and eliminating outliers from the response data set;

(g) determining the optimal number of factors;

(h) detecting and eliminating outliers within training set;

(i) analyzing training set using multivariate regression to produce a regression set;

(j) validating said regression set to produce a predictive set for a predictive calibration model.

28. A process according to claim 27, wherein said electrolyte solution is selected from the group consisting of:

an electroplating bath;

an electroless plating bath;

an electrowinning bath;

an electrorefining bath;

an electroforming bath;

an electromicromachining bath; or

an electropolishing bath.

29. A process according to claim 27, wherein said sample data set of step (a) is obtained by design of experiment (DOE) routines.

30. A process according to claim 29, wherein said DOE routine is multi-component multilevel linear orthogonal array.
31. A process according to claim 29, wherein said DOE routine is multicomponent multilevel fractional factorial.
32. A process according to claim 29, wherein the electroanalytical response of step (b) is obtained by DC Voltammetry.
33. A process of claim 32, wherein the DC Voltammetry technique is selected from the group consisting of:

DC Cyclic Voltammetry;
DC Linear Scan Voltammetry;
DC Anodic Stripping Voltammetry;
DC Cathodic Stripping Voltammetry;
DC Adsorptive Stripping Voltammetry;
DC Cyclic Voltammetric Stripping technique;
or combinations thereof.

34. A process according to claim 27, wherein the electroanalytical response of step (b) is obtained by a technique selected from the group consisting of:

DC Staircase Voltammetry;
Normal Pulse Voltammetry;
Reverse Pulse Voltammetry;
Differential Pulse Voltammetry;
Square Wave Voltammetry;
AC Voltammetry;
Chronoamperometry;

Chronopotentiometry;
Electrochemical Impedance Spectroscopy technique;
Polarographic techniques;
or combinations thereof.

35. A process according to claim 27, wherein said electroanalytical response of step (b) comprises a plurality of data points.

36. A process according to claim 27, wherein said electroanalytical response of step (b) is a combination of one or more portions of a complete electroanalytical response.

37. A process according to claim 27, wherein said electroanalytical response of step (b) comprises a combination of one or more portions of independent electroanalytical responses.

38. The method of claim 27, wherein step (d) comprises autoscaling the data to unit variance.

39. The method of claim 38, wherein autoscaling the data to unit variance comprises the steps of:

performing mean centering; and
dividing by the standard deviation.

40. The method of claim 27, wherein step (e) comprises the steps of:

1) analyzing the data using correlation coefficient calculations based on the least squares regression;
2) analyzing the data using SIMCA based calculations of modeling power; and
3) analyzing the data using a product of said correlation coefficient and said modeling power.

41. The method of claim 27, wherein step (f) comprises analyzing the data using a technique selected from the group consisting of:

principle component analysis;

Mahalanobis distance;

Mahalanobis distance coupled with principal component analysis;

Mahalanobis distance coupled with principal component analysis with Q residuals;

SIMCA;

or further combinations thereof.

42. The method of claim 27, wherein step (g) comprises analyzing the data using PRESS analysis.

43. The method of claim 42, wherein said PRESS analysis is based on PCR calculations.

44. The method of claim 42, wherein said PRESS analysis is based on PLS calculations.

45. The method of claim 27, wherein step (g) comprises analyzing the data using Exner psi function calculations.

46. The method of claim 45, wherein said Exner psi function analysis is based on PCR calculations.

47. The method of claim 45, wherein said Exner psi function analysis is based on PLS calculations.

48. The method of claim 27, wherein step (h) comprises analyzing the data using a technique selected from the group consisting of:

F^C -ratio analysis;

Studentized concentration residuals analysis;
leverages analysis; and
coupled Studentized concentration residuals analysis and leverages analysis.

49. The method of claim 27, wherein step (i) comprises analyzing the data using a technique selected from the group consisting of PLS and PCR.

50. A process according to claim 27, wherein said validation step (j) is accomplished through internal validation and external validation.

51. A process according to claim 50, wherein said internal validation uses cross validation comprising the following steps:

- (1) omitting a single sample from said training set, thereby creating a new training set;
- (2) analyzing said new training said using decomposition and multivariate regression method to produce a new regression data set;
- (3) predicting said omitted sample target component concentration using said new regression data set;
- (4) returning sample to the training set;
- (5) repeating steps (1) through (4) until all individual samples were treated;
- (6) determining an R^2 value for said predicted samples based on said predicted and said known concentrations; and
- (7) validating said training data set if said R^2 value is above about 0.95; and repeating steps (a) to (j) if said R^2 value is less than about 0.95.

52. A process according to claim 50, wherein said internal validation uses cross validation comprising the following steps:

- obtaining a second sample set comprises an electrolyte solution of known composition;
- obtaining an electroanalytical response for each sample of said second sample set;

predicting said target component concentration for each sample of said second sample set using said predictive calibration model;

determining an R^2 value for all samples of said second sample set based on said predicted and said known concentrations;

validating said predictive calibration model if said R^2 value is above about 0.95; and repeating steps (a) to (j) if said R^2 value is less than about 0.95.

53. A process to predict the concentration of target constituent in an electrolyte solution, said process comprising:

(a) producing a predictive data set, the predictive data set generated by:

(a1) obtaining a sample set, wherein each sample comprises an electrolyte solution of known composition;

(a2) obtaining an electroanalytical response for each said sample to produce an electroanalytical response data set;

(a3) obtaining a training set that comprises said sample set and corresponding said electroanalytical response data set;

(a4) analyzing said training set using decomposition and multivariate regression method to produce a regression data set;

(a5) validating said training data set to produce said predictive data set for a predictive calibration model.

(b) using said predictive data set to predict the concentration of target constituent, said concentration predicted by:

(b1) obtaining an unknown sample set, wherein each unknown sample in said unknown sample set contains an electrolyte solution;

(b2) obtaining an electroanalytical response for each said unknown sample to produce an electroanalytical response data set;

(b3) preprocessing of said electroanalytical response data set; and

(b4) applying said predictive calibration model to predict concentration of target component in each said sample.

54. A process to create a predictive data set, which can be employed to the other systems to predict the amount of a target constituent in an electrolyte solution, said process comprising:

(a) producing a predictive data set on a primary system by:

(a1) obtaining a primary sample set, wherein each sample comprises an electrolyte solution of known composition;

(a2) obtaining a primary electroanalytical response for each said sample to produce an electroanalytical response data set;

(a3) obtaining a primary training set that comprises said primary sample set and corresponding said primary electroanalytical response data set;

(a4) preprocessing the primary training set;

(a5) determining the calibration range;

(a6) detecting and eliminating outliers from the primary response data set;

(a7) determining the optimal number of factors;

(a8) detecting and eliminating outliers within said primary training;

(a9) analyzing primary training set using multivariate regression to produce a regression set;

(a10) validating said primary training set to produce a predictive set for a predictive calibration model.

(b) producing a transformation data set for a secondary system, said process comprising:

(b1) obtaining a secondary sample set that is a subset of said primary sample set;

(b2) obtaining an electroanalytical response for each said secondary sample to produce an electroanalytical secondary response data set;

(b3) obtaining secondary-to-primary transformation data set.

(c) using said transformation data set and primary predictive data set to predict the concentration of target constituent for a secondary system said process comprising:

(c1) obtaining an unknown sample set, wherein each unknown sample in said unknown sample set contains an electrolyte solution;

(c2) obtaining an electroanalytical response for each said unknown sample by the secondary system to produce an electroanalytical response data set;

(c3) applying said transformation data set and primary predictive data set to predict a concentration of target constituent in each said sample.

55. The method of claim 54, wherein step (b3) is selected from the group consisting of:

Direct Standardization technique;

Direct Standardization coupled with PCA technique;

Piecewise Direct Standardization technique;

Direct Standardization with Additive Background Correction technique;

Direct Standardization with Additive Background Correction coupled with PCA technique;

Piecewise Direct Standardization with Additive.